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(בעברית) (Hebrew) **תא אלקטרוכימי נטען**

(באנגלית) (English) **CHARGEABLE ELECTROCHEMICAL CELL**

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This 09 of September of the year 1999

Signature of the Applicant חתימת המבקש

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P-2684-IL

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CHARGEABLE ELECTROCHEMICAL CELL

תא אלקטרוכימי נטען

Eitan, Pearl, Latzer & Cohen-Zedek

P-2684-IL

Chargeable Electrochemical Cell

FIELD OF THE INVENTION

This invention relates to a flexible design for accumulators, fuel cells and electrolyzers based on super light and super strong conductive and insulative materials in the form of special woven fabrics. This design may withstand very heavy overloads (property weight) at high accelerations of up to 50,000 g. As a result, there is an increase in kinetic uses of such accumulators. The same is true for insulation and cell materials which can be provided in a monolithic design. This kind of design can withstand accelerations of up to 55,000 g i.e., known products including artillery shells. The drastic decrease by 10-50 times in distance between electrodes in lead acid accumulators with the resulting decrease in internal resistance of the accumulator (principal part of internal accumulator resistance) creates an element with high electrical efficiency. The used active material permits to realize deep cycle charge – twice that of accumulators with semi-rigid electrodes- discharge and realized capacity of accumulator at multicycle work. A specific electrode material layout permits using pairs of electrode materials with dendrite problems for multicycle battery. The invention is suitable for lead-acid or silver-zinc accumulators, fuel cells, and electrolyzers, where weight and cost are important parameters.

BACKGROUND OF THE INVENTION

The problem of the high specific weight of accumulators, fuel cells and electrolyzers arises from the use of heavy metal electrodes, such as lead, silver, zinc, platinum, etc. These metals have very high densities and low mechanical strengths. Discharge depth is limited by electrode strength since active materials also have a structural function in electrodes.

These metals also have high active surface areas. A specific surface area of special electrodes such as porous electrodes or slurry or powder electrodes, is advantageous and may be used with or without a catalytic plate.

Some electrode pairs, such as zinc - silver, also have dendrite problems. As a result, dendrite induced short circuits limit the number of cycles during the life of a rechargeable battery.

An object of this invention is to decrease the weight and increase the strength of accumulator, fuel cell and electrolyzer electrodes. A design using carbon paper is described in U.S. Patent 4,894,355. This patent proposes to decrease the active surface area by cutting the ends of the fibers which consist of a carbon paper/polytetraflouroethylene composition. In this case, the main load of design takes carbon carrier material - paper, and conductivity parameters, determines thickness and span of electrode.

SUMMARY OF THE INVENTION

One object of this invention is to combine the conductivity or insulation parameters with a high strength/low weight ratio in one unit. Active and/or catalytic materials may be used in plate form (catalytic fuel cell or electrolyser) or in friable form (accumulator). This latter form permits a better use of the chemically active material without weakening the electrode's structure. The efficiency of the electrodes is increased as a result of enhanced intergranular contact induced by a spring element and/or by the battery's outer casing. The invention unifies these parameters and as a result there is a decrease in weight per discharged energy.

According to the invention, the battery cell comprises a flexible envelope in which a flat electrically conductive flexible wire or fabric grid is embedded in a matrix of granular or powder particles of an active material. Another envelope is also present containing an electrically conducting wire or fabric grid on which grains or particles of a complementary active metal or compound are positioned. The envelopes are separated by an insulating membrane which is permeable to the ions of a suitable electrolyte. There are conductive leads from each of the battery's cells. There is also a flexible spring element that supplies the required pressure to counteract the electrode's volume changes resulting from the chemical reaction in the cell.

The active material can be placed in a membrane bag or between sheets. The grains of active material can be fixed in position as distinct units by welding the cover.

The present invention provides a means for applying pressure to the external surface of the assembled cell, ensuring close contact during charging and discharging between the granular or powder particles and between the particles and the electrode. This contact is maintained despite significant volume changes of the active material during the reaction.

Various pairs of metals or compounds can be used, such as Ni/Cd, Ag/Zn, Pb/PbO, etc.

The electrodes can be fabricated in the form of lengthy ribbons which can then be rolled into a spiral configuration. In such a design, it is advantageous to provide a spring to apply pressure to the external surface of the cells and to fabricate the cells in cylindrical form.

The spring element may be an entirely separate element included in the battery. Alternatively, the flexibility of the battery cell's walls can function as the spring element. A separate spring element is best suited for flat batteries where cell wall height is limited. The side walls of the cell are best suited to serve as the spring element when the cell has a cubic, or at least rectangular, shape. Flexible outer cylindrical containers can function as the spring element for cells with helical electrodes.

The powder or grains of the active material are preferably in the 5 to 10 micron range, although other sizes can be used.

The sheet grids may be made from expanded metals, such as gold. These are manufactured from expanded metal foil relevant to the active material of the cathode or anode. Conductive fabric thickness is generally about 10 μ to 500 μ with the preferable thickness being about 100 μ. The fabric can be woven from carbon fibers. Conductive materials may be coated

with suitable metals, the exact metal depending on the nature of the electrochemical couple in the cell and the environment in which the cell operates.

For multicell versions, the conductive fabric may also be used in combination with non-conductive fibers. In such conductive fabrics, a plurality of parallel carbon fibers interwoven with fibers of Kevlar, nylon, polyester, etc. can be used. The configuration may be such that each carbon fiber constitutes an electrode. It is clear that the carbon fibers must be connected and a conductor lead provided for the current output.

A modification of the invention based on the same concept comprises fuel cells in which each membrane bag contains catalyst particles preferably attached to a suitable support. The catalyst may be in the form of ceramic particles coated with an active material, such as Ni, Pt or Cd. A suitable acid can serve as a catalyst in the fuel cell with oxygen and hydrogen reacting to form water and produce electric current. Suitable electrode connections are provided for current uptake. In the case of fuel cells, no external pressure on the cell is required. A catalyst may be directly plated on the carbon fibers increasing the active surface area.

Due to the thin elements of the novel electrochemical cells, the weight to power output is improved. Since the main elements of the cells are a conductive fabric, granular active material, suitable membranes and an electrolyte, the cells can withstand extreme accelerations and decelerations without detrimental effect on cell performance.

A high energy, high speed chargeable battery cell can be produced when provided in a helical configuration.

According to this invention, electrodes, connection elements and cell walls are made from high-strength, conductive or insulative fibers/fabrics, catalyst, and active material in plate or friable form or the like. Carbon fibers may be used as the conductive part of electrodes while for the insulative parts, nylon, polyester, Kevlar or glass fibers can be used. The exact choice of insulative material depends on the electrolyte chosen.

Different designs can be used depending on the electrochemical principles. Parts should be designed to obtain stable electrical contact, resulting in conductivity in friable forms of the active material. Similarly, there should be adequate contact between the active material and the current input-output elements.

Suitable designs can include:

1. Electrodes, insulation elements, spring and outer cell casing made from separate parts and assembled into a single unit.

2. Electrodes and insulation elements in one unit. One piece of fabric woven in accordance with the need for the combination of conductivity and insulation or conductivity, insulation and active materials.

Different electrolytic principles of accumulator design may be realized in the first group of design.

Determination of some of the parameters suggests the following design specifications: a fiber thickness of 10 μ, a fabric thickness of 0.05, a specific area for the electrode of 31.5cm^2 per 1 cm^2 of electrode geometry area. This is without special surface treatment to increase the microsurface.

The active area per unit weight in this case is 1875 cm^2/g. i.e. 1100 times greater than a solid surface.

Additional specifications include conductivity cross-section per span distance, 0.0157 cm^2/cm, electrical resistance, 0.4 -0.5 $ohm*mm^2$, and a permissible stress of 50 kg/mm^2 given a fabric density of 168 g/m^2 i.e. a maximum destroying length of 30 km. In comparison, lead has a value of is 0.122 km, zinc 0.63 km and copper 2.263 km. Therefore, a coated graphite fiber electrode can withstand acceleration 15 times greater than a copper electrode and 300 times greater than a lead electrode for electrodes of equal lengths.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is herein described, by way of example only, with reference to the accompanying drawings, wherein:

Figure 1 is a sectional view of the configuration of an accumulator of the Zn -Air or Zn- Ag type with anodes of the Zn - ZnO or Zn – AgO or Ag - ZnO slurry type

Figure 2 is a sectional view of the design of a Zn-Air accumulator cell or one with Zn - Ag pairs with anodes of the Zn - ZnO or Zn – AgO or Ag - ZnO slurry type

Fig. 2a is a sectional view.

Figure 3 is a sectional view of a spiral design for the electrode couple.

Figure 4 illustrates a parallel or serial connection between cells.

Figure 5 illustrates a multicell "one piece design" of a special fabric.

Figure 6 illustrates multi-electrodes and multicells made from one piece of special fabric.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Reference is now made to FIG. 1. Figure 1 is a sectional view of an example of a unit cell of fabric with central coaxially displaced fabric conductivity elements.

Electrode conductive element 1 (cathode or anode) is a woven carbon fiber fabric. In this case, the fibers do not need a special treatment to increase their microsurface.

Electrode housing 3 has a flat piece of conductive fabric 2 inserted into the electrical insulation bag 5 filled with a zinc, lead or silver oxide slurry 2 on both sides of the conductive element 1.

The electrode bag 6 and both layers 2 are pressed together by a spring and intake are in separate insulation chamber 5 executed from electrolyte permeability insulation fabrics which represents an accumulator element.

Figure 2 is a sectional view of a design of a unit cell of fabric. Electrode conductor 1 (cathode or anode) is woven from carbon fibers. Again, the fibers do not require special treatment to increase their surface area.

Electrode conductor 1 is made from a zinc, lead or silver oxide slurry 2.

Electrode bag 1 can be provided with lattice or diagonal seams 7 to avert agglomeration of the slurry powder into a single piece. This helps to ensure an adequate powder distribution on the electrode surface. The electrode bag and both intakes are in separate insulation chambers 3 made of electrolyte permeable insulation fabrics.

The insulation chambers may be changed and divided into pieces of fabrics, which may be sewn to form an electrode bag from the sides of a pair of electrodes. The sewing threads may be made of insulating material.

A couple of these insulated electrodes (cathode and anode) have one difference: the consistency of slurry 2. In an accumulator design the electrode pair or set of electrode pairs may be held under pressure by spring elements 8 of a different form. This saves the pressure needed for electrical contact between slurry and conductive fabric and between separate slurry nucleus (about 0.5 kg/cm_2). However, this pressure supply needs structural integrity.

The electrode couple is located in a common shell 4 and constitutes a single cell. Shell 4 may be produced from flexible or rigid plastic materials like polyethylene, polypropylene, polyurethane or PVC. This material may be reinforced with glass, polyester, Kevlar, etc. fibers. The connection of all elements into a single unit may be done by heat welding at 5. The free electrode ends 6 may be used for the electrical connection of the cell.

The shape of the electrode and its position in a battery cell may vary. Among the various alternatives which can be used in a plate electrode with trim placing or a circular electrode in a coaxial structure. Electrolyte may be stored permanently in shell 4 or supplied periodically by special welding tubes.

Figure 3 is a sectional view of a spiral design for electrodes. A pair of flexible electrodes 1 and 2 of the form shown Figure 1 or Figure 2 are rolled into a spiral and inserted into an elastic sleeve 3, the latter serving as a spring element to ensure adequate contact pressure (0.5 kg/cm2). The rolled spiral with spring elements is inserted into outer housing 4. In principle, the outer housing may also serve as the spring elements in some embodiments.

Figure 4 illustrates a connection between cells which can be connected, serially or in parallel. Some electrode bags which are meant to be

connected can be made from a single piece of conductive fabric. In this case, all conventional connection parts are excluded decreasing accumulator weight and complexity and increasing reliability.

Figure 5 illustrates a one piece multi-electrode design which consists of a special fiber combination with a trim conductivity and insulation fiber or group of fibers, for use as electrode insulation or connecting elements. This trim may be different for weft and warp, for different accumulator designs, or because of weave problems.

The one-piece multi-electrode design includes a conductive part of electrode 1 made from conductive fibers and an insulative part 2 made of insulative fibers. Conductive parts of fabrics may also be used in conjunction with cross conductive thread stripes, which can connect electrode parts.

For a better connection between electrode parts and the connection strip, the connection may be preliminarily plated and welded.

The trim of conductive parts does not determine what kind of electrode (cathode or anode) may be connected and what type of connection, parallel or series, should be used.

These parameters may be chosen as in common battery designs, where a one piece multi-electrode fabric is a common element that permits different designs and electrical configurations of accumulators, fuel cells, or electrolyzers.

The fabric may have a one-sided coating of PVC, polyethylene, polypropylene or polyurethane, for welding with other layers of the design, and outer shell formation. In this case, conductive fibers must be first treated to permit adhesion to the coating material.

Figure 6 illustrates a design that can be realized with a multi-electrode one piece fabric. This design is an example of a slurry electrode accumulator with serial connection of separate cells. The design consists of two one-piece multi-electrode units 1, separated by an electrolyte permeable fabric 2 that can be sewn or welded separately from the electrode design piece.

The welding seams position is in a form that provides insulation of separate cells formation with intake and outlet channels if a flow electrolyte system is used and permeability of outer space.

EXAMPLES

Example #1

Battery layout	Flat
Battery active material	Silver - Zinc
Number of cells in battery	2
Battery voltage	3 volt
Battery capacity	5AH
Battery housing thickness	5.4 mm
Battery housing area	18.5 cm^2
Electrode particle diameter	0.005-0.01mm^2
Silver electrode thickness	0.8 mm
Zinc electrode thickness	0.92 mm
Silver weight	19.45g
Zinc weight	11.78g
Weight of total active material	31.23g
Weight of conductive material	1.90g

Weight of insulation material	1.64g
Weight of electrolyte, KOH	21.4g
Weight of accessories	37.1g
Total weight of battery	88.77

Example #2

Battery layout	Flat
Active material	Silver - Zinc
Number of cells per battery	16
Battery voltage	24 volt
Battery capacity	100AH
Battery housing thickness	200mm
Battery housing area	200 cm^2
Electrode particle diameter	0.005-0.01 mm^2
Silver electrode thickness	0.8 mm
Zinc electrode thickness	0.92 mm
Silver weight	3169g
Zinc oxide weight	2023g
Weight of total active material	5192g
Weight of conductive material	93.5g
Weight of insulation material	215g
Weight of electrolyte, KOH	2545 g
Weight of accessories	765g
Total weight of battery	8810 g

Example #3

Battery layout	Flat
Battery active material	Lead
Number of cells in battery	6
Battery voltage	12 volt
Battery capacity	60 AH
Battery housing thickness	150 mm
Battery housing area	120cm^2
Electrode particle diameter	0.005-0.01mm^2
Anode thickness	0.8 mm
Cathode thickness	0.92 mm
Lead weight	6,300g
Lead oxide weight	7,100g
Weight of total active material	13,400g
Weight of conductive material	421g
Weight of insulation material	85g
Weight of electrolyte, acid	1110g
Weight of accessories	521g
Total weight of battery	15,452g

Example #4

Battery layout	Spiral
Battery active material design	Silver - Zinc
Number of cells in battery	1
Battery voltage	1.5-1.8 volt

Battery capacity	15 AH
Battery spiral diameter	30mm
Battery spiral height	27mm
Electrode particle diameter	0.01 mm^2
Silver electrode thickness	0.8 mm
Zinc electrode thickness	0.92 mm
Silver weight	45.32g
Zinc weight	11.78g
Weight of total active material	57.1 g
Weight of conductive material	1.90g
Weight of insulation material	1.64g
Weight of electrolyte, KOH	28.9g
Weight of accessories	19.5g
Total weight of battery	109.04g

What is Claimed is:

1. A rechargeable electrochemical battery cell comprising a closed housing in which there are positioned two units which differ only in the active material, each such unit comprising a flat flexible bag of an ion conductive insulating material (membrane) containing a flat, conductive fabric electrode and from both its sides a powder form active material, an electrolyte, where each electrode is connected with a conductor leading to the outside for current uptake, means being provided for maintaining pressure from granule to granule and from granule to electrode fabric for needed electrical contact.

2. A cell according to claim 1, which for decreasing dendrite hazards has a conductor executed in the first form of a flexible electrically conducting envelope which contains a flexible conductive support of active material in powder or grain form,

the second electrode being also in the form of a flexible electrically conductive envelope containing an electrically conductive support on which there is a layer of an electrochemically complementary active material, flexible ion-conductive membrane sheet positioned between the two envelopes, and means for exerting pressure on the assembly of electrode separator sheet or membrane/counterelectrode so as to maintain these in close contact with each other, said assembly being immersed in a suitable electrolyte, electrode connections being provided from each of the envelopes.

3. A cell according to claim 1 or 2, where the electrode fabric is woven and pleated active materials is a flexible electrically conducting fabric mainly of carbon fibers and other active material fibers.

4. A cell according to any of claims 1 to 3, where the active material pair is one of the following: Ni/Cd, Ag/Zn, Pb/PbO.

5. A cell according to any of claims 1 to 4, where the support is a flexible fabric comprising a sequence of adjacent parallel conductive and insulating stripes.

6. A cell according to any of claims 1 to 5, where the thickness of each electrode is between about 1 and 10mm.

7. A cell according to any of claims 1 to 6, where the particles of the active material are of a grain size of between about 1 and 10 microns, in a 1 to 3mm thick layer with or without a suitable matrix.

8. A cell according to any of claims 1 to 7, where the thickness of the fabric is between about 10 and 100 microns.

9. An electrochemical cell according to any of claims 1 to 8, where the cell is wound in a helical configuration with an external spring applying a pressure on the assembly.

10. An electrochemical cell according to any of claims 1 to 9, having high mechanical strength comprising a high-strength, porous, micron pore size fabric separator.

11. A modified cell according to claim 1, being a fuel cell, where catalytically active material is supported by a ceramic sheet, the reaction being an interaction of oxygen and hydrogen producing water and energy.

12. A fuel cell according to claim 11, where a catalyst is plated on a conductive fabric with high surface area.

13. A cell according to any of claims 1 to 10, where the electrode comprises parallel fibers of carbon and fibers of active material, such as carbon and silver.

14. A cell according to any of claims 1 to 3, where the active material is preliminarily pressed under medium pressure to achieve a porosity of 50-60% in the bulk condition, and where said active material is pressed under flexible low pressure when said cell is fully assembled.

15. A cell according to claim 14 where the preliminary pressure used is about 100 to 200 kg/cm^2 and where the low pressure used is about 1 to 5 kg/cm^2.

16. A cell according to any of claims 1 to 3, where the electrode's flexible conductive support positioned in the bulk active material is made from a flexible thin grid material, where such grid material is of the expanded type.

17. A cell according to claim 16, where the material of the grid is suitable for anodes made of cadmium, zinc, tin or indium and/or cathodes of nickel or silver.

18 A cell according to any of claims 1 to 3, where the electrode's flexible conductive support positioned in the active material is made of woven graphite fibers, said fibers coated with metal to suppress gas evolution.

19. A cell according to claim 18 wherein the thickness of the metal coating applied to suppress gas evolution is 5 to 15 microns.

20. A cell according to claim 18, wherein the cell is a silver-zinc rechargeable cell and where the metal coating used is nickel or silver for the cathode and tin, indium, cadmium, lead, or zinc for the anode.

21. A cell according to claim 18, where the coating consists of two layers, a solid protective layer of 95-99% solidity and a second layer of 30-60% porosity.

22 A cell according to any of claims 1 to 3 wherein the means for exerting pressure is the outer container of the cell, said container having an elasticity needed to maintain a pressure adequate to ensure electrical contact within the assembled cell.

23. A cell according to any of claims 1 to 3, wherein the cell is a spiral type cell and wherein the means for exerting pressure is executed as a central flexible rod.

24. A cell according to any of claims 1 to 3, wherein the separator consists of two layers, the first layer imparting mechanical strength to the separator and made from a nylon, polypropylene or polyethylene treated woven fabric and the second layer preventing whisker penetration made of an ion separation polyethylene – polypropylene film and executed in the form of a closed bag.

25. A cell according to any of claims 1 to 3, wherein one of the electrodes has a semi-rigid consistency, said semi-rigid consistency having a porosity of 30-50 %, and said electrode executed by sintering, pressing or other method.

26. A cell according to claim 25, wherein the cell is a secondary silver-zinc cell and wherein the electrode formed as in claim 25 is the silver electrode.

27. A cell accoruing to any of claims 1-26 substantially as described hereinabove.

28. A cell according to any of claims 1 - 26 substantially as illustrated in any of the drawings.

For the Applicant

Eitan, Pearl, Latzer & Cohen Zedek
Advocates, Patent Attorneys & Notaries
P-2684-IL

ABSTRACT

An electrochemical cell for batteries comprising one or more pairs of electrodes. The first electrode is comprised of a flexible electrically insulating and ion conducting envelope which contains a flexible conductor. This flexible conductor can be made of a conductive fabric, inserted into an active material in granular or powder form. The second electrode is also a flexible electrically insulating envelope containing an electrical conductor inserted into a layer of an electrochemically complementary active material. The cell also contains a means for applying pressure to the assembly of electrodes, the membrane separator, and the counterelectrodes so as to maintain contact between the active material particles and the conductor. The assembly also contains a suitable electrolyte; electrode connections are provided from each of the envelopes. The particles of the active material are generally of a grain size between about 5 to 10 micron and in a 0.3 to 3mm thick layer, with or without a suitable matrix. The thickness of the conductive flexible material including the fabric is generally between about 100 to 300 microns. In other cases, the active material may be plated on the conductor surface. For high mechanical strength a high strength porous, micron pore size fabric separator is preferably used.

The form, positioning, pressure and orientation needed for electrical contact of the electrode's free, powdery, active material is achieved by pressure induced contact arising from a spring element. This spring element

can be a separate element or associated with the elasticity of the walls of the cell. The spring should compensate for volume changes in the electrode resulting from the chemical reaction occurring within the battery.

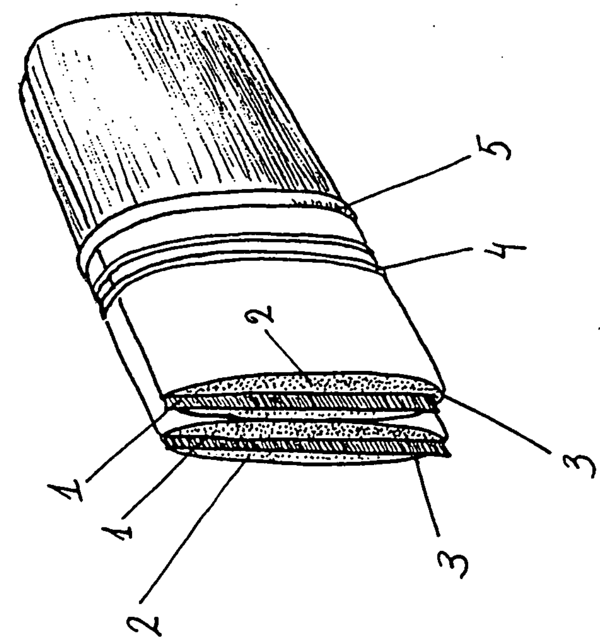

Fig. 1

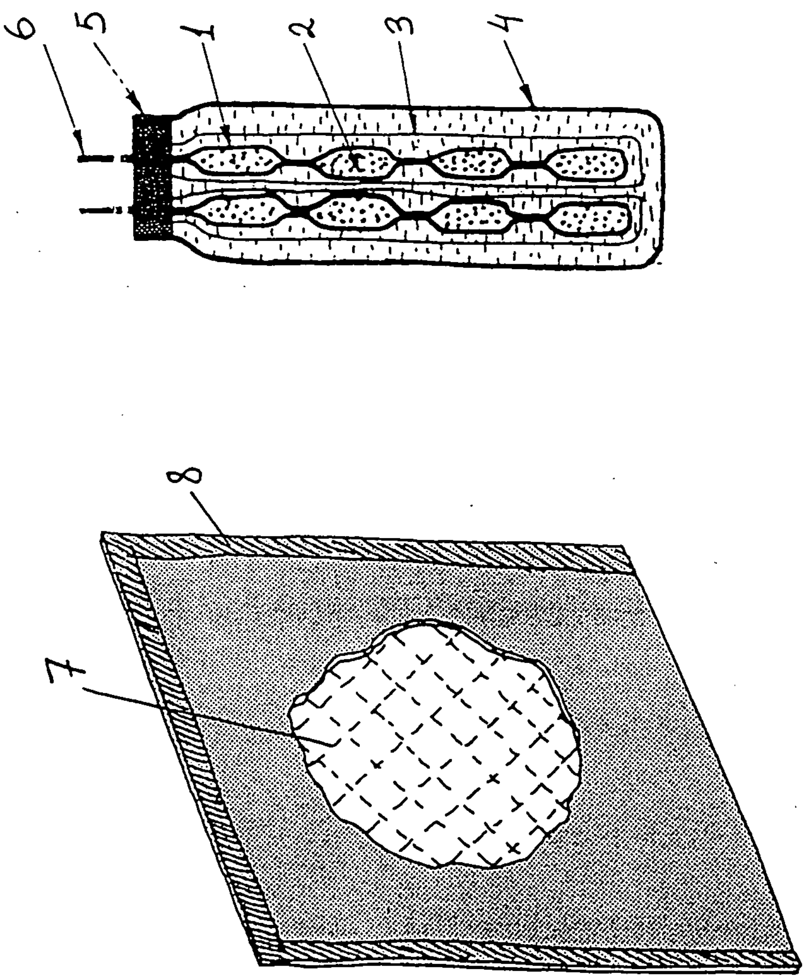

Fig. 2

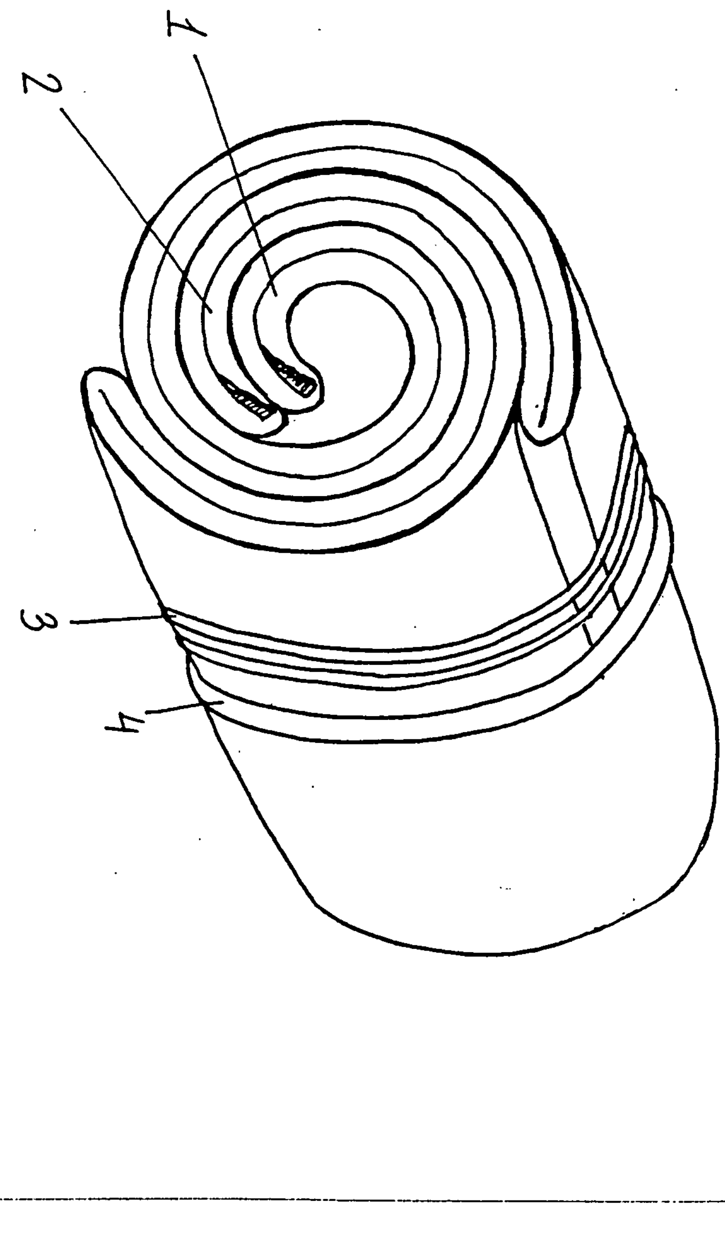

Fig. 3

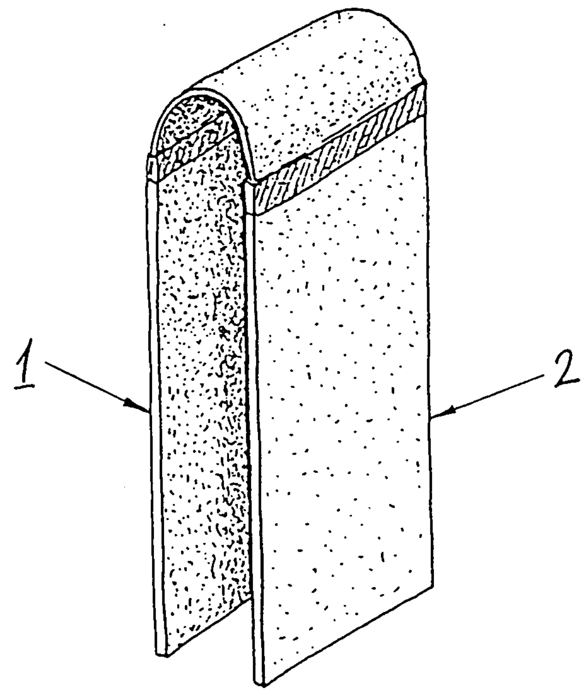

Fig. 4

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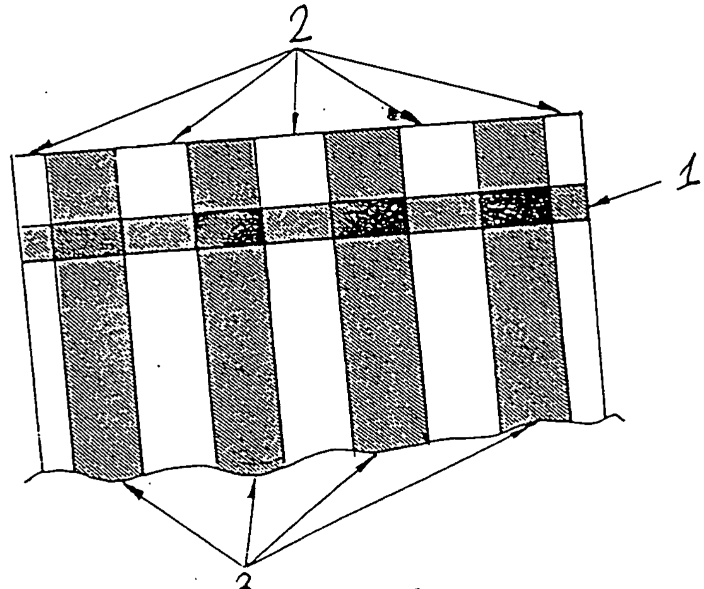

Fig. 5

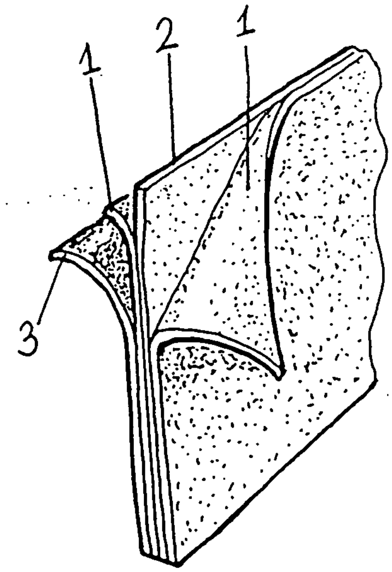

Fig. 6